$PM_{2.5}$ SAMPLING AND CHARACTERIZATION PROGRAM IN LIBRARY, PA

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INTRODUCTION

Particles with a mean aerodynamic diameter of ca. 45 µm or less, known as total suspended particulate (TSP), have been of concern to the health community since the 1950s. In July 1997, the EPA proposed its most restrictive ambient air standard for particle matter. This standard applies to particles with a mean aerodynamic diameter of 2.5 µm or less ($PM_{2.5}$). It sets an annual limit for $PM_{2.5}$ of 15 µg/m^3, averaged over three years, and a 24 h limit of 65 µg/m^3 (98th percentile, averaged over three years). In supporting documentation for the recommendation to implement this new standard, EPA stated that SO_2 (a precursor to the formation of secondary sulfate particles) is a key source of $PM_{2.5}$, and of concern to human health. EPA also stated that the SO_2 is predominantly generated by the combustion of fossil fuels, especially coal. Another class of compounds which EPA stated to be a major component of $PM_{2.5}$ and also of concern to human health is nitrates derived from NOx generated in the combustion of fossil fuels. In addition to regulations based on alleged health effects, in an effort to regulate $PM_{2.5}$, EPA also proposed draft regional haze regulations that focus on the impact of $PM_{2.5}$ on visibility impairment in Class I ("pristine") areas of the United States. The scientific bases for these standards are now under review.

CONSOL R&D began a sampling program in January 1997 in Library, PA (thirteen miles south of Pittsburgh, PA) to measure the concentration of $PM_{2.5}$ particles collected from the air and to characterize the components of the collected samples. This paper describes the sampling methods, data collected, and conclusions drawn from this program.

At the time CONSOL began its sampling program, no federal reference method (FRM) had been established for the collection of fine particles 2.5 µm or smaller. At CONSOL, the initial samples were collected using cyclone samplers. CONSOL R&D has a great deal of experience using cyclones for the collection of particles from stationary source stack sampling work.

In July 1997, EPA published an FRM for $PM_{2.5}$ collection; the method requires the use of impactors, not cyclones. CONSOL added a Graseby-Andersen FRM single channel sampler to the on-site $PM_{2.5}$ sample collection effort being performed with the cyclones. Later, a Graseby-Andersen sequential $PM_{2.5}$ sampler was employed. Collection with both the cyclones and the Graseby-Andersen samplers continued until January 1999, at which time the use of the cyclones was discontinued. The samplers were collocated (within four feet of each other). Weather data also were collected on the CONSOL Library, PA, site beginning June 1998.

EXPERIMENTAL

Prior to 1997, the procedures used to acquire samples with cyclone samplers were those used primarily for sampling of stack gases.[1] The cyclones used for this work provide a particle size cut (with a mean diameter of 2.5 µm, D_{50}) within the range of 0.1-10 µm.[3] Two types of filter material were used, Teflon™ and quartz. Quartz filters are difficult to weigh because they fluctuate in weight with changes in humidity. However, they were used for selected samples to eliminate carbon background, which would interfere in the anticipated carbon analyses. Procedures for sample collection and determination of $PM_{2.5}$ concentration with the FRM samplers is detailed in the Code of Federal Regulations 40 Part 50 Appendix L. The FRM specifies the use of Teflon™ filters. Field blanks were acquired; field blank weights are one to two orders of magnitude smaller than sample weights.

Collected samples were weighed and randomly selected samples were analyzed for sulfate, nitrate, chloride, and ammonium by ion chromatography (IC). Quartz filters were reserved for carbon analyses.

RESULTS AND DISCUSSION

Comparison of Cyclone to FRM Sampler Collected Filter Samples

Two cyclones were collocated with the single-channel Graseby-Andersen FRM sampler for thirteen months. $PM_{2.5}$ concentrations were calculated from the mass of particles collected on the filters and the air flow rate through the filters. Figure 1 shows good correlations ($R^2 = 0.967$ and $R^2 = 0.942$) between the $PM_{2.5}$ concentrations measured in the same 24 h period using the two sample collection devices. The slopes of the two lines on Figure 1 are 0.96 and 1.07 for cyclones 1 and 2, respectively.

Seasonal and Daily Variations

$PM_{2.5}$ concentrations for all samples collected outdoors in the period of January 1997 through August 1999 are shown in Figure 2. Some variations with the seasons can be observed. The $PM_{2.5}$ concentration in ambient air averages 20.0 µg/m³ throughout the two and one half plus years of the outdoor sampling program, excluding high ozone days. Ozone action days (designated as open points) were declared by the Pennsylvania Department of Environmental Protection (DEP). The average $PM_{2.5}$ concentration for high ozone days was 42.3 µg/m³. $PM_{2.5}$ concentrations were examined for variations according to day of the week (Table 1). Because of the large standard deviations, little variation is observed. The range of $PM_{2.5}$ concentrations is roughly equivalent regardless of the day of the week.

Variations in $PM_{2.5}$ Concentration with Weather Data and Ozone Concentration

Total $PM_{2.5}$ concentration was examined as a function of weather data (temperature, barometric pressure, rainfall, and humidity). A trend with weather data is evident only in the relationship of $PM_{2.5}$ and temperature. $PM_{2.5}$ concentration is higher on days when the temperature exceeds 80 °F. The $PM_{2.5}$ concentration distribution shifts to higher values for samples acquired at ≥80 °F (Figure 3).

$PM_{2.5}$ concentrations are plotted as a function of ozone concentrations acquired by the Pennsylvania State DEP at a location 17 miles southeast of Library, PA (Charleroi, PA). $PM_{2.5}$ concentrations increase with increasing ozone concentration (Figure 4); this is consistent with the work of Chu and Cox[2]. It cannot be definitively determined from these data whether the higher $PM_{2.5}$ concentration levels are a result of higher temperature, the higher ozone concentrations, or other confounding effects.

$PM_{2.5}$ Composition

Sixty-four filter samples collected from January 1997 through August 1998 were analyzed for sulfate, nitrate, ammonium, and chloride. The average composition for particles collected on non-ozone action days is: 32 wt % sulfate, 11 wt % ammonia, 7.5 wt % nitrate, 3.0 wt % chloride and 46 wt % organic and inorganic carbon and mineral matter. The average composition for samples collected on ozone action days is: 48 wt % sulfate, 14 wt % ammonia, 1.5 wt % nitrate, 2.2 wt % chloride, and 34 wt % carbon and mineral matter (Table 2).

The concentration of sulfate (µg/m³) in the $PM_{2.5}$ collected on non-ozone days was in the range of 0.8 to 16.0 µg/m³. On ozone action days, the range of $PM_{2.5}$ sulfate concentrations was 7.4 to 35.5 µg/m³. There is a general increase in sulfate and ammonia concentration in the summer months and an apparent decline in concentration of nitrates. The highest chloride concentrations were found in particles collected in June and July.

Sulfates and nitrates exist in the atmosphere as aerosols. When reacted with ammonia, they form fine particles that can precipitate. Thus, the form of the sulfates and nitrates in the particles is likely to be ammonium salts. Several ammonium salts are possible (ammonium sulfate, $(NH_4)_2SO_4$, ammonium bisulfate, $(NH_4)HSO_4$ and ammonium nitrate, NH_4NO_3). In addition, chlorides would likely be found as ammonium chloride (NH_4Cl). The correlation between the concentration (µmole/m³) of ammonium and the concentration (µmole/m³) of sulfate in the $PM_{2.5}$ collected on all days is good ($R^2 = 0.94$). The ammonium and sulfate mole ratios may provide a clue to which ammonium sulfate salt predominates in the particulate matter. Two assumptions were made in the data analysis; they are: 1) all Cl^- and NO_3^- are present as ammonium salts, and 2) all SO_4^{2-} is present as an ammonium salt. The mole ratios of NH_4^+ (residual) to SO_4^{2-}, after accounting for the Cl^- and NO_3^-, range from -0.2 to 2.0. The average value is 1.3. Thirty-nine percent of the filter samples have an NH_4^+/SO_4^{2-} ratio of 1.6 to 2.0 and 47% have a ratio of 1.0 to 1.5. From the limited number of samples and the limited data analysis, it is likely that both ammonium sulfate and ammonium bisulfate are present in the particulate matter.

CONCLUSIONS

A fine particle matter ambient air sampling program has been conducted on the CONSOL R&D sit in Library, PA, (south of Pittsburgh, PA) for almost three years. Particles with an aerodynamic mean diameter of 2.5 µm or less ($PM_{2.5}$) were collected using two types of sampling equipment, cyclones, and impactors. The two kinds of sampling equipment when collocated were found to collect the same mass of particles in the same time. The collected samples were analyzed using several methods. In conjunction with the particulate matter collection, weather data also were obtained for a portion of the sampling program duration. Total $PM_{2.5}$ concentration was found to vary slightly with season and vary little with day of the week, changing significantly (greater than one standard deviation from the mean of the non-ozone days) only on days of high ambient air ozone concentrations and temperatures greater than 80 °F. The magnitude of the effect of either of these linked variables on the concentration of $PM_{2.5}$ cannot be determined from the data presented here. However, because the effect is strong, the importance of including these and other confounding variables in $PM_{2.5}$ ambient air studies and $PM_{2.5}$ related health effect studies is indicated. The average $PM_{2.5}$ ambient air concentration for all days in which samples were acquired is 20.0 µg/m^3. On non-ozone action days, the average $PM_{2.5}$ concentration is 17.8 µg/m^3. Neither of these concentrations would meet the proposed EPA limit of 15 µg/m^3. The concentration of sulfate found (on average) for all days (33%) is approximately that found by EPA (34.1%) in $PM_{2.5}$ acquired in the eastern U.S.[3] Further studies, which include compositional analyses of many more samples collected from sites around the eastern U.S., are required to confirm this result. A good correlation was found between the ammonium and sulfate concentrations in the particles indicating the possibility that the sulfate is resident in the particles as ammonium salts.

REFERENCES

1. Recommended Methodology for the Determination of Particle Size Distributions in Ducted Sources; Project final report to The California Air Resources Board; ARB Contract A3-092-32; Southern Research Institute, May 1986.
2. Chu, S.-H.; Cox, W. M. "Relationship of PM fine to Ozone and Meteorology", Presented at the Air & Waste Management Association 91st Annual Meeting & Exhibition, San Diego, CA, June 14-18, 1998.
3. U.S. EPA "Air Quality Criteria for Particulate Matter". EPA/600/P-95-001aF-cF, Washington, DC, April 1996.

Table 1. $PM_{2.5}$ Concentration Ranges, Averages, and Standard Deviations for Non-Ozone Action Days, Sorted by Day of the Week

	Number of Samples	Range Low	Range High	Avg	Std Deviation
Monday	25	8.0	48.9	18.6	11.7
Tuesday	48	2.4	38.5	14.2	8.5
Wednesday	41	10.1	51.3	19.2	7.9
Thursday	75	2.3	46.9	18.6	8.1
Friday	12	5.9	28.4	17.2	6.5
Saturday	25	7.2	33.5	15.5	8.1
Sunday	26	6.2	34.7	18.6	8.4

Table 2. Average Concentration (wt %) of Components in $PM_{2.5}$ Samples

	All Samples (a)		Non-Ozone Action Days (b)		Ozone Action Days (c)	
Component, wt %	average	σ	average	σ	average	σ
Sulfate	33	13	32	12	48	7.9
Ammonium	11	3.2	11	3.3	14	2.0
Nitrate	7.0	19	7.5	20	1.5	1.3
Chloride	2.9	3.9	3.0	4.0	2.2	1.1
Balance (d)	46		46		34	

a) Total of all samples analyzed: 63
b) Total of non-ozone action day samples analyzed: 54
c) Total of ozone action day samples analyzed: 9
d) Includes Inorganic and Organic Carbon and Minerals

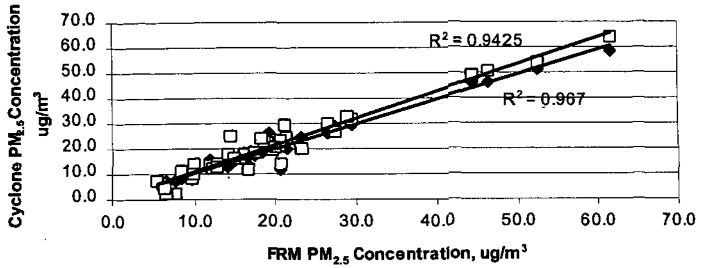

Figure 1. Comparison of $PM_{2.5}$ Concentration Measured in Cyclones 1 (solid points) and 2 (open points) with the Single-Channel FRM Sampler.

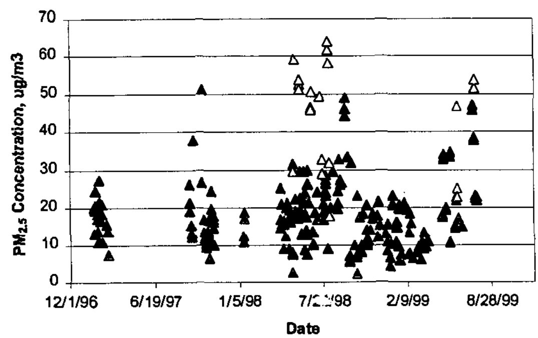

Figure 2. $PM_{2.5}$ Concentration - CONSOL R&D Library, PA 1/27/97 – 7/30/99 (Open Points are Ozone Action Days).

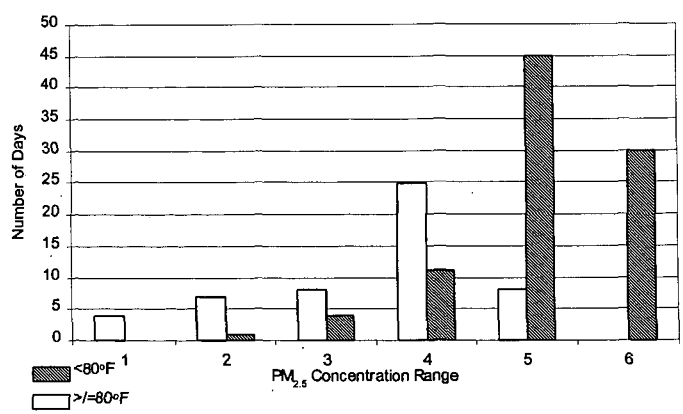

Figure 3. Change of $PM_{2.5}$ Concentration Distributions with Different Outside Daily High Temperature Ranges.
($PM_{2.5}$ Concentration Ranges (μg/m³): 1 = 50⁺; 2 = 40-50; 3 = 30-40; 4 = 20-30; 5 = 10-20; 6 = 0-10)

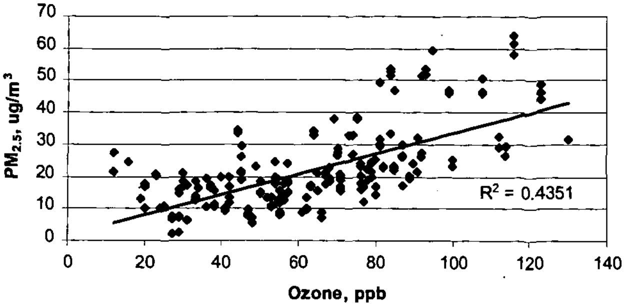

Figure 4. $PM_{2.5}$ Concentration Measured in Library, PA vs. Ozone Concentration Measured in Charleroi, PA